

We claim:

1. A hard capsule comprising

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(A) polymers obtainable by free-radical polymerization of

- 10 a) at least one vinyl ester of C<sub>1</sub>-C<sub>24</sub>-carboxylic acids  
in the presence of  
15 b) polyether-containing compounds and  
c) where appropriate one or more other copolymerizable  
monomers c) and subsequent at least partial  
hydrolysis of the ester functions in the original  
monomers a),

20 with the proviso that in the absence of another  
copolymizable monomer c) the polyether-containing compound  
b) must have a number average molecular weight ≤ 10,000,

(B) where appropriate structure-improving auxiliaries and

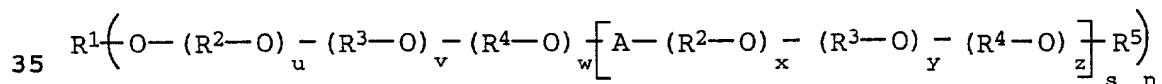
(C) other conventional constituents.

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2. A hard capsule as claimed in claim 1, wherein the polymers  
(A) are obtainable by free-radical polymerization of

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- a) at least one vinyl ester of C<sub>1</sub>-C<sub>24</sub>-carboxylic acids in  
the presence of  
35 b) polyether-containing compounds of the general formula I



40 in which the variables have, independently of one  
another, the following meaning:

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R<sup>1</sup> hydrogen, C<sub>1</sub>-C<sub>24</sub>-alkyl, R<sup>6</sup>-C(=O)-, R<sup>6</sup>-NH-C(=O)-,  
polyalcohol residue;

R<sup>5</sup> hydrogen, C<sub>1</sub>-C<sub>24</sub>-alkyl, R<sup>6</sup>-C(=O)-, R<sup>6</sup>-NH-C(=O)-;

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R<sup>2</sup> to R<sup>4</sup>

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- (CH<sub>2</sub>)<sub>2</sub>-, - (CH<sub>2</sub>)<sub>3</sub>-, - (CH<sub>2</sub>)<sub>4</sub>-, - CH<sub>2</sub>-CH(R<sup>6</sup>)-,  
-CH<sub>2</sub>-CHOR<sup>7</sup>-CH<sub>2</sub>-;

R<sup>6</sup> C<sub>1</sub>-C<sub>24</sub>-alkyl;

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R<sup>7</sup> hydrogen, C<sub>1</sub>-C<sub>24</sub>-alkyl, R<sup>6</sup>-C(=O)-, R<sup>6</sup>-NH-C(=O)-;

A -C(=O)-O, -C(=O)-B-C(=O)-O,  
-C(=O)-NH-B-NH-C(=O)-O;

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B - (CH<sub>2</sub>)<sub>t</sub>-, arylene, optionally substituted;

n 1 to 1000 (1-200);

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s 0 to 1000 (0-200);

t 1 to 12 (1-12);

u 1 to 5000 (1-250);

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v 0 to 5000 (0-250);

w 0 to 5000 (0-250);

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x 0 to 5000 (0-250);

y 0 to 5000 (0-250);

z 0 to 5000 (0-250);

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and

c) where appropriate one or more other copolymerizable monomers

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and subsequent at least partial hydrolysis of the ester functions in the original monomers a), with the proviso that b) in the absence of c) has a number average molecular weight between 300 and 10,000, and n-z have the values stated in

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parentheses.

3. A hard capsule as claimed in either of claims 1 or 2, wherein the polymers (A) are obtainable by free-radical polymerization of

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a) at least one vinyl ester of C<sub>1</sub>-C<sub>24</sub>-carboxylic acids in  
the presence of

b) polyether-containing compounds of the general formula I  
with a number average molecular weight of from 300 to  
100,000, in which the variables have, independently of  
one another, the following meaning:

R<sup>1</sup> hydrogen, C<sub>1</sub>-C<sub>12</sub>-alkyl, R<sup>6</sup>-C(=O)-, R<sup>6</sup>-NH-C(=O)-,  
polyalcohol residue;

R<sup>5</sup> hydrogen, C<sub>1</sub>-C<sub>12</sub>-alkyl, R<sup>6</sup>-C(=O)-, R<sup>6</sup>-NH-C(=O)-;

R<sup>2</sup> to R<sup>4</sup>

- (CH<sub>2</sub>)<sub>2</sub>- , - (CH<sub>2</sub>)<sub>3</sub>- , - (CH<sub>2</sub>)<sub>4</sub>- , - CH<sub>2</sub>-CH(R<sup>6</sup>)-,  
- CH<sub>2</sub>-CHOR<sup>7</sup>-CH<sub>2</sub>- ;

R<sup>6</sup> C<sub>1</sub>-C<sub>12</sub>-alkyl;

R<sup>7</sup> hydrogen, C<sub>1</sub>-C<sub>12</sub>-alkyl, R<sup>6</sup>-C(=O)-, R<sup>6</sup>-NH-C(=O)-;

n 1 to 8;

s 0;

u 2 to 2000 (2-250);

v 0 to 2000 (0-250);

w 0 to 2000 (0-250);

and

c) where appropriate one or more other copolymerizable  
monomers

and subsequent at least partial hydrolysis of the ester  
functions in the original monomers a), with the proviso that

b) in the absence of c) has a number average molecular weight  
between 300 and 10,000, and u-w have the values stated in  
parentheses.

4. A hard capsule as claimed in any of claims 1 to 3, wherein  
the polymers (A) are obtainable by free-radical  
polymerization of

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- a) at least one vinyl ester of C<sub>1</sub>-C<sub>24</sub>-carboxylic acids in  
the presence of  
5 b) polyether-containing compounds of the general formula I  
with a number average molecular weight of from 500 to  
50,000, in which the variables have, independently of one  
another, the following meaning:

10 R<sup>1</sup> hydrogen, C<sub>1</sub>-C<sub>6</sub>-alkyl, R<sup>6</sup>-C(=O)-, R<sup>6</sup>-NH-C(=O)-;

R<sup>5</sup> hydrogen, C<sub>1</sub>-C<sub>6</sub>-alkyl, R<sup>6</sup>-C(=O)-, R<sup>6</sup>-NH-C(=O)-;

R<sup>2</sup> to R<sup>4</sup>

15 - (CH<sub>2</sub>)<sub>2</sub>-, - (CH<sub>2</sub>)<sub>3</sub>-, - (CH<sub>2</sub>)<sub>4</sub>-, - CH<sub>2</sub>-CH(R<sup>6</sup>)-,  
-CH<sub>2</sub>-CHOR<sup>7</sup>-CH<sub>2</sub>-;

R<sup>6</sup> C<sub>1</sub>-C<sub>6</sub>-alkyl;

20 R<sup>7</sup> hydrogen, C<sub>1</sub>-C<sub>6</sub>-alkyl, R<sup>6</sup>-C(=O)-, R<sup>6</sup>-NH-C(=O)-;

n 1;

s 0;

25 u 5 to 1000 (5-250);

v 0 to 1000 (0-250);

w 0 to 1000 (0-250);

30 and

- c) where appropriate one or more other copolymerizable monomers

35 and subsequent at least partial hydrolysis of the ester functions in the original monomers a), with the proviso that b) in the absence of c) has a number average molecular weight between 300 and 10,000, and u-w have the values stated in 40 parentheses.

- 45 5. A hard capsule as claimed in any of claims 1 to 4, wherein the polymers (A) are obtainable by free-radical polymerization of

- a) at least one vinyl ester of C<sub>1</sub>-C<sub>24</sub>-carboxylic acids in the presence of
- b) polyether-containing compounds and
- c) where appropriate 0 to 20% by weight of one or more other copolymerizable monomers

and subsequent at least partial hydrolysis of the ester functions in the original monomers a), wherein the polyether-containing compounds b) have been prepared by polymerization of ethylenically unsaturated alkylene oxide-containing monomers, and, where appropriate, other copolymerizable monomers.

- 15 6. A hard capsule as claimed in any of claims 1 to 5, wherein if at least one other copolymerizable monomer c) is present it is selected from the group:
  - acrylic acid, methacrylic acid, maleic acid, fumaric acid,
  - crotonic acid, maleic anhydride and its monoesters, methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, n-butyl acrylate, n-butyl methacrylate, t-butyl acrylate, t-butyl methacrylate, isobutyl acrylate, isobutyl methacrylate, 2-ethylhexyl acrylate, stearyl acrylate, stearyl methacrylate, N-t-butylacrylamide, N-octylacrylamide, 2-hydroxyethyl acrylate, hydroxypropyl acrylates, 2-hydroxyethyl methacrylate, hydroxypropyl methacrylates, alkylene glycol (meth)acrylates, styrene, unsaturated sulfonic acids such as, for example,
  - acrylamidopropanesulfonic acid, vinylpyrrolidone, vinylcaprolactam, vinyl ethers (for example: methyl, ethyl, butyl or dodecyl vinyl ether), vinylformamide, vinylmethylacetamide, vinylamine, 1-vinylimidazole, 1-vinyl-2-methylimidazole, N,N-dimethylaminomethyl methacrylate and N-[3-(dimethylamino)propyl]methacrylamide;
  - 3-methyl-1-vinylimidazolium chloride,
  - 3-methyl-1-vinylimidazolium methyl sulfate,
  - N,N-dimethylaminoethyl methacrylate,
  - N-[3-(dimethylamino)propyl]methacrylamide quaternized with methyl chloride, methyl sulfate or diethyl sulfate.
- 7. A hard capsule as claimed in any of claims 1 to 6, wherein the ratios of amounts are
  - 45 a) 10 to 98% by weight
  - b) 2 to 90% by weight

- c) 0 to 50% by weight.
8. A hard capsule as claimed in any of claims 1 to 7, wherein  
the ratios of amounts are  
5  
a) 50 to 97% by weight  
b) 3 to 50% by weight  
c) 0 to 20% by weight.
- 10 9. A hard capsule as claimed in any of claims 1 to 8, wherein  
the ratios of amounts are  
a) 65 to 97% by weight  
b) 3 to 35% by weight  
15 c) 0 to 20% by weight.
10. A hard capsule as claimed in any of claims 1 to 9, wherein  
the resulting polymers are subsequently crosslinked by a  
polymer-analogous reaction.  
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11. A hard capsule as claimed in any of claims 1 to 10, wherein  
dialdehydes, diketones, dicarboxylic acids, boric acid, boric  
acid salts, and salts of multiply charged cations are  
employed for the subsequent crosslinking.  
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12. A hard capsule as claimed in any of claims 1 to 11, wherein  
the structure-improving auxiliaries (B) employed are the  
following classes of compounds:  
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a) polymers with a molecular weight greater than 50,000  
b) substances which lead to crosslinking of the polymer  
chains of the polymers,  
35  
c) and, where appropriate, substances which lead to  
crosslinking of the polymer chains of the  
structure-improving auxiliaries.
13. A hard capsule as claimed in any of claims 1-12, wherein the  
40 structure-improving auxiliaries employed are polymers from  
the following classes of substances:  
45 polyamino acids such as gelatin, zein, soybean protein and  
derivatives thereof, polysaccharides such as starch, degraded  
starch, maltodextrins, carboxymethylstarch, cellulose,  
hydroxypropylmethylcellulose, hydroxypropylcellulose,  
hydroxyethylcellulose, methylcellulose,

carboxymethylcellulose, ethylcellulose, cellulose acetate,  
cellulose acetate phthalate, hydroxypropylcellulose acetate  
phthalate, hydroxypropylcellulose acetate succinate,  
hemicellulose, galactomannans, pectins, alginates,  
5 carageenans, xanthan, gellan, dextran, curdlan, pullulan,  
gum arabic, chitin, and derivatives thereof, synthetic  
polymers such as polyacrylic acid, polymethacrylic acid,  
copolymers of acrylic esters and methacrylic esters,  
polyvinyl alcohols, polyvinyl acetate, polyethylene glycols,  
10 polyoxyethylene/polyoxypropylene block copolymers,  
polyvinylpyrrolidones and derivatives thereof.

14. A hard capsule as claimed in any of claims 1 to 13, which  
comprises as other conventional shell constituents fillers,  
15 release agents, flow aids, dyes, pigments, opacifiers,  
flavorings, sweeteners, plasticizers, preservatives and/or  
active ingredients.
15. A hard capsule as claimed in any of claims 1 to 14, wherein  
20 the shell consists of 10 to 100% polymers of vinyl esters or  
polyether, where appropriate 0 to 80% structure-improving  
auxiliaries and, where appropriate, 0 to 30% other  
conventional constituents.
- 25 16. A hard capsule according to any of claims 1 to 15, obtainable  
by the dip process.
17. A hard capsule as claimed in any of claims 1 to 16, which  
comprises one or more active pharmaceutical ingredients,  
30 vitamins, carotenoids, minerals, trace elements, food  
supplements, cosmetic active ingredients, crop protection  
agents, bath additives, perfume, flavoring, cleaner or  
detergent.
- 35 18. A hard capsule as claimed in any of claims 1 to 17, wherein  
the shell comprises from 20 to 80% of a polymer resistant to  
gastric fluid.
19. A hard capsule as claimed in any of claims 1 to 18, wherein a  
40 coating resistant to gastric fluid is applied using  
pharmaceutically customary coating processes to achieve  
resistance to gastric fluid after production.
20. The use of the hard capsule as claimed in any of claims 1 to  
45 19 for pharmaceutical applications.

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21. The use of the hard capsule as claimed in any of claims 1 to 19 for cosmetic applications, applications in crop protection, or for cleaners or food supplements.

5 22. The use of polymers obtainable by free-radical polymerization of

a) at least one vinyl ester of C<sub>1</sub>-C<sub>24</sub>-carboxylic acids in the presence of

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b) polyether-containing compounds and

c) where appropriate one or more copolymerizable monomers

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and subsequent at least partial hydrolysis of the ester functions in the original monomers a), with the proviso that b) in the absence of c) has a number average molecular weight between 300 and 10,000 for producing a hard capsule as claimed in any of claims 1 to 19.

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